

CENTRIFUGAL LENGTH SEPARATION OF CARBON NANOTUBES

CROSS REFERENCES TO RELATED APPLICATION

[0001] The present application claims priority from U.S. provisional patent application Ser. No. 60/939,915 filed May 24, 2007.

FIELD OF INVENTION

[0002] The presently disclosed embodiments are directed to the field of carbon nanotubes, and particularly to methods for separating carbon nanotubes and isolating particular populations of carbon nanotubes.

BACKGROUND OF THE INVENTION

[0003] Scalable nano-manufacturing of single wall carbon nanotube (herein periodically referred to as "SWCNT") devices, sensors, and therapeutic agents require precursors that exhibit well-defined length, chirality, and dispersion characteristics. However, existing synthetic and dispersion methods for SWCNTs produce heterogeneous mixtures of tube diameters, lengths and chiralities. As the unique optical, physical, thermal and electronic properties of SWCNTs arise from the specific chiral wrapping vector of the graphene sheet, the necessity for separation of SWCNT materials by chirality is readily appreciated. However, the strength and usability of chirality specific properties also depends strongly on the length of the nanotube, and thus length fractionation is also desirable or required for many applications. The cost-effectiveness of performing both of these separations will determine the future utility of technologies based upon SWCNTs.

[0004] The economical separation of SWCNTs by length and wrapping vector is an area of substantial ongoing research. Length separation has been carried out using various chromatographic techniques, including gel electrophoresis and size exclusion chromatography (SEC), which yield populations possessing well-defined lengths and length distributions. For example, U.S. Pat. No. 7,131,537 describes methods for separating nanotubes by size. The separation methods produce fractions of nanotubes with different lengths. However, the separation methods are all chromatography based. The patent indicates that gel permeation chromatography is preferred, see col 4, lines 1-3.

[0005] While SEC methods are scalable in principle, lengths have been limited in practice by the exclusion limit of the column stationary phase, which is generally less than 600 nm. Accordingly, it would be desirable to separate and isolate populations of SWCNTs by length, using techniques that were not limited to such relatively small lengths and which enabled separation and isolation of populations having significantly greater lengths.

[0006] Since the development of high speed ultracentrifugation in the early twentieth century, the separation of solutes with weak buoyancy differences has been feasible due to the enormous centripetal acceleration generated by such instruments. Separations by centrifugation to obtain nanotubes have been described by various artisans, such as in the following patents. U.S. Pat. No. 5,560,898 discloses a process of isolating carbon nanotubes from a mixture of nanotubes and graphite particles, by centrifuging a dispersion of the material in a liquid medium. After centrifuging, the nanotubes are left

in the liquid medium, while the graphite particles are in a precipitate. However, the nanotubes are not further separated in any manner. U.S. Pat. No. 7,029,645 describes a method for "cleaning" a carbon nanotube sample by dispersing it in an organic solvent, and then centrifuging to separate the nanotubes from the impurities. However, the collected "cleaned" nanotubes are not further separated by size or any other characteristic.

[0007] The use of ultracentrifugation on SWCNTs within a density gradient to produce a more facile and scalable chirality separation was described by Arnold et al., in "Sorting Carbon Nanotubes by Electronic Structure Using Density Differentiation," *Nature Nanotech*, 1, 60-65 (2006) (herein referred to as "Arnold et al."). This work is based upon driving the SWCNTs to their individual equilibrium locations within the density gradient. That is, Arnold et al. demonstrated the use of ultracentrifugation to produce chirality separation of different diameter nanotubes by driving the position of the SWCNTs to their different isopycnic (equilibrium buoyancy) locations within a density gradient. However, Arnold et al. did not provide any strategies for separation of SWCNTs according to their length.

[0008] Recently, several methods have been described to enhance SWCNT population purity of individual SWCNT species. These methods include electrophoresis, dielectrophoresis, and ion exchange chromatography, which have all been demonstrated to separate tubes by diameter and electronic structure, although with limited throughput. Although satisfactory in certain respects, a need remains for a commercially scalable process for purifying one or more SWCNT species. It would also be beneficial to provide such processes that were economical. And, as will be appreciated, it would be particularly desirable to provide a method for large scale and economical separations of these species by length.

[0009] Increasingly, efforts at separation are incorporated with purification efforts, for the removal of non-SWCNT carbon and metallic residues, and the individualization of the nanotubes via surfactant dispersion. Surfactant dispersion, whether using small molecule surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl-benzyl sulfate (NaDDBS), biological molecules such as DNA, or bile salts such as either sodium cholate (NaChol) or sodium deoxycholate (DOC) typically involves two steps, sonication of the SWCNTs in the presence of the surfactant, and centrifugation to remove the less buoyant material, including much of the catalyst and amorphous carbon impurities. Again, although satisfactory in certain aspects, a need remains for a strategy by which SWCNTs can be readily separated, purified, and isolated. And, it would be particularly desirable to provide techniques for such operations that could be readily performed at a commercial scale where economics and high throughput are primary objectives.

SUMMARY OF THE INVENTION

[0010] The difficulties and drawbacks associated with previous methods and associated systems are overcome in the present method and system for a strategy by which carbon nanotubes can be separated by length.

[0011] In a first aspect, the present invention provides a method for separating carbon nanotubes by length. The method comprises providing carbon nanotubes having different lengths and dispersing the nanotubes in a suitable medium to solubilize the nanotubes and thereby form a first liquid. The method further comprises preparing a second liquid having